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PROCESS FOR LEACHING ACID-CONSUMING ORES

RELATED APPLICATION

This application claims priority of United States Provisional Patent Application Serial No. 60/430,618 filed December 2, 2002, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to methods for leaching metals from low sulphur content ores and more particularly to a process where fine elemental sulphur is preconditioned for a period of time with sulphur oxidizing bacteria in a reactor and the reactor products are added to an ore heap during agglomeration so that sulphuric acid will be produced directly at the reactive mineral sites to attack the ore and dissolve its contained metallic content.

2. DISCUSSION OF THE RELATED ART

Statutory Invention Registration (SIR) document number H2,005 published November 6, 2001, discloses a process for leaching low sulphur content materials, in particular ores. While this publication may not constitute prior art to the present invention, it discloses a process for leaching low sulphur materials, in particular ores, for the recovery of metals contained in them, comprising leaching low sulphide materials with a leaching agent produced by bacterial oxidation of a second material with sulphur oxidizing bacteria, to liberate metal values from the low sulphur ores. Essentially, the process

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disclosed is a single-state process. In the example illustrated in Fig. 1 of the SIR, the low sulphur content material constitutes secondary copper ore which is crushed and brought into contact with sulphur, water and bacteria. The water and bacteria act on the sulphur to oxidize it into sulphuric acid, which then attacks and dissolves the secondary copper ore, liberating copper.

International Application WO 01/36693 A3 describes a similar process, where elemental sulphur and sulphur oxidizing bacteria are added to a heap of oxide ores and where the sulphuric acid produced by the bacterial oxidation of the sulphur dissolves metals from the ore. U.S. Patent 6,610,268 describes a process where molten sulphur is coated onto a carrier material which is subsequently treated with sulphur oxidizing bacteria in order to produce sulphuric acid.

It is believed that these processes produce relatively low concentrations of sulphuric acid. The biological oxidation of elemental sulphur is notoriously slow; in general, it is believed that the rates of acid production in these processes are too slow for commercial application.

SUMMARY OF THE INVENTION

The present invention relates to a two-step process. In the first step elemental sulphur, a sulphur oxidizing bacteria and water are reacted in a stirring tank for an extended period such as 12-24 hours. The elemental sulphur used in this process is preferably rod milled to produce the largest possible surface area to enable maximum bacterial attachment. For example, rod milling 1.9 kilograms of sulphur in 1 liter of water for 15 minutes produced

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+400 mesh 52.2%, -400 mesh 47.8%. The sulphur oxidizing bacteria preferably includes a culture of *Thiobacillus thiooxidans* alone, or along with other sulphur oxidizing bacteria including thermophilic bacteria.

This preconditioning step causes the highly hydrophobic elemental sulphur to become fully wetted allowing the bacteria present to attach themselves to the surface of the sulphur particles. At the same time a quantity of sulphuric acid, normally 20-40 g/L, is produced in the reaction, which can be used to partially satisfy the acid demand of the ore by adding the acid during agglomeration of the ore as well as by adding some of the acid to the leach solution reservoir.

In the second step of my process the fine sulphur preconditioned with water and the bacteria is added to the ore during the typical agglomeration process used to adhere the small ore particles to the large ore particles, a process commonly employed to increase the permeability of the ore heap produced. By obtaining a homogeneous distribution of the sulphur in the heap, acid will be produced directly at the reactive mineral sites and will be consumed immediately, thus maintaining a relatively low acid concentration in the heap and therefore a low driving force for the acid/alkaline gangue reactions. This low driving force results in lower overall acid consumption than that encountered in typical acid leaching, where a strong acid front moves downwardly in the heap or dump.

In addition, producing acid homogeneously in the heap greatly enhances copper extraction rates. In a typical conventional acid leach of an

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oxide ore, most of the applied leach solution travels nearly vertically downward through the ore mass, with only a small amount of solution traveling at a slow rate in the horizontal plane. For reactions to take place in the ore not directly located in the downward flow of solution, it is necessary for acid to diffuse to the reaction sites, a notoriously slow process. It is generally agreed the very limited extent of such diffusion significantly reduces the rate of copper extraction in oxide copper leaching operations. However, in my method, where acid is produced at the mineral reaction sites, homogeneously throughout the heap, such diffusion is no longer required and the overall extraction rate is significantly increased.

Thiobacilli are highly sensitive to changes in their environment, e.g., a 0.2 instant change in pH can put the bacteria in severe shock. When acid and bacteria are added to an acid-consuming ore, typically the acid/gangue reactions at the mineral surfaces cause a significant increase in the pH of the interstitial leach solution, thus causing significant bacterial inhibition. In my process, approximately 5-25% of the acid demand of the ore is added during the agglomeration step. This acid can be sulphuric acid, preferably acid produced in the reactor during the sulphur preconditioning step of my process. I believe that this acid reacts with the alkaline components of the ore, causing a thin layer of neutralization products such as CaSO₄ to cover the reactive surfaces, thus slowing down the acid/gangue reaction speed and therefore allowing for the rapid development of the bacteria. This acid will also

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neutralize some of the extremely reactive gangue material that may be present, thus helping to stabilize the pH of the interstitial solutions.

The preconditioning process also produced a quantity of acid solution at a pH of less than 1.0, which can be used to satisfy part of the ore's acid demand during agglomeration.

The bacteria require certain nutrients in order to grow at rapid rates, such as encountered in agitated reactors. There are several well known nutrient solutions available. It is my experience that use of the 9K nutrient solution disclosed in the Journal of Bacteriology, 1959a, 77, 642 gives optimum results in my process, but only when the ferrous iron is deleted and the amount of ammonium reduced to 10% of the stated amount. Other objects, advantages and applications of my present invention will be made apparent by the following detailed description of a preferred embodiment of my invention. The description makes reference to the accompanying drawings in which:

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plot of the extraction profile for a column test on 40 kg of -½ inch ore which consumes 28 kg acid per tonne when leached with sulphuric acid;

Fig. 2 is a plot of another column, operated with non-preconditioned sulphur, showing a lower leach rate than the column employing the preconditioned sulphur;

Fig. 3 is a plot showing the effective partial acid demand satisfaction on the leach rate of a group of columns; and

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Fig. 4 is a plot of the extraction curves for two columns showing the commercial significance of my invention.

DETAILED DESCRIPTION OF THE INVENTION

In the preconditioning step of my process, the finely rod-milled elemental sulphur, along with water, is subjected to a culture of sulphur oxidizing bacteria, preferably including or limited to a culture of *Thiobacillus thiooxidans*, for 12-48 hours in an agitated reactor. During this preconditioning period, the sulphur particles become fully wetted, allowing the bacteria present to attach themselves to the surface of the sulphur particles.

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The bacteria used are preferably *Thiobacillus thiooxidans* but can include additionally other sulphur oxidizing bacteria, including thermophilic bacteria. However, I have found that once the sulphur in the agglomerated ore started to produce sulphuric acid, and the pH of the solution emanating from the bottom of the ore pile has decreased to the range of 2.4-1.8, the addition to the ore of an actively growing culture of *Thiobacillus ferrooxidans* greatly enhances subsequent copper extraction. It has been shown that the rate of oxidization of ferrous iron by *Thiobacillus ferrooxidans* decreases rapidly with decreasing pH. However, in the heap or dump, the pH in the ore mass can be controlled to be in the range of 1.8-2.4 so that *Thiobacillus ferrooxidans* can significantly assist in the sulphur oxidation process as well as oxidized secondary copper sulphides such as chalcocite. I believe that *Thiobacillus ferrooxidans* participates in the production of sulphuric acid from elemental sulphur by oxidizing the intermediate sulphur oxidation products resulting

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from the actions of *Thiobacillus thiooxidans*. Because of the inhibition of *Thiobacillus ferrooxidans* at pH values below 1.6, I have not added this bacterium to the preconditioning reactor, as the pH of the sulphur suspension often reaches as low as 0.8.

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In the second step of my process, sulphur produced by preconditioning with water and the bacteria is added to the ore during the typical agglomeration process used to adhere the smaller particles to the large particles. The advantages of this process as previously stated are realized.

TEST RESULTS

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Fig. 1 shows the extraction profile for a column test on 40 kg of -1/2 inch ore which consumes 28 kg acid per tonne when leached with sulphuric acid. Here I added only 2.3 kg/T acid during agglomeration as well as 300 grams of elemental sulphur, equivalent to

 $100/40 \times 300/1000 = 7.5 \text{ kg/T sulphur}.$

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 $7.5/32 \times 98 = 23 \text{ kg/T sulphuric acid.}$

Column 7 was inoculated with *Thiobacillus thiooxidans* only, through the preconditioned sulphur added. Column 10 had both *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* added. I believe that the improved extraction is due mainly to *Thiobacillus ferrooxidans* assisting in the sulphur oxidation process. Although *Thiobacillus ferrooxidans* is not known as an elemental sulphur oxidizer, I believe that it oxidizes the partial oxidation products resulting from the action of *Thiobacillus thiooxidans*.

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Tail assays on the residue from these columns show that Columns 7 and 10 had 0.077% and 0.080% chalcopyrite copper respectively, proving that *Thiobacillus ferrooxidans* did not contribute by oxidizing chalcopyrite. In addition, comparison of the head and tail copper sulphide assays shows that Columns 7 and 10 had produced 32% and 30% copper sulphide oxidation respectively. This oxidation relates to the more readily oxidizable sulphides such as chalcocite and covelite. Since both columns had similar sulphide oxidation, we can conclude that *Thiobacillus ferrooxidans* did not contribute by directly oxidizing these sulphides either. It is more likely that ferric iron was the oxidizing agent involved.

In Fig. 2 is shown that Column 14, operated with non-preconditioned sulphur, does indeed leach slower than Column 10, which had been treated with preconditioned sulphur. Column 10 reaches 70% extraction in approximately 55 days, whereas Column 14 takes 80 days to reach a similar extraction. That is 45% longer. In a commercial heap leach operation, that would mean a 45% larger leach pad area, involving considerable extra cost.

In Figure 3 are shown the results of four 45 kg column tests of a 25 kg/T acid consuming ore, where Column 5 had 7.1 kg/T acid added during agglomeration. Column 7 had 2.3 kg/T added, Column 8 had 1.5 kg/T and Column 9 only 0.8 kg/T acid added. The resultant extraction curves show clearly that the leaching process is significantly enhanced when part of the acid demand of the ore is satisfied at the start of the leach.

The commercial significance of my invention is clearly demonstrated in Fig. 4, where the extraction curves are shown for two columns, each containing 1,162 kg of a 28 kg/T acid-consuming ore. These columns were 18 feet high and only 1.5 kg/T biologically produced acid was added at the start of the leach. *Thiobacillus ferrooxidans* was added after 27 days, when the pH of the solution leaving the bottom of the columns reached 2.6. 70% extraction was reached after only 100 days.

Having disclosed my invention I claim: